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On the Lowering of the Tensile Strength of Cotton Fiber Caused by the Intermolecular Crosslinking*

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It is well known that the tensile strength of cotton fiber is remarkably lowered, when intermolecular crosslinking is given to cotton fabric to increase its crease recovery. To find the fundamental principle to improve this disadvantage, the author investigated the mechanism from the molecular structural standpoint using chiefly the results of our researches. Considering the fact that this phenomenon did not occur in rayon, it was presumed that the molecular mechanism of the lowering of the tensile strength of cotton or flax fibers by intermolecular crosslinking might be as same as that of the abnormal phenomenon of increasing their tensile strength by water wetting. It has been found that the abnormality of wet tensile strength was disappeared with the decrease of the degree of polymerization or crystallinity, so it was presumed that those variations of fine structure might have something to do with the problem of the lowering of the tensile strength of cotton by the intermolecular crosslinking. Preliminary, some good effects were found by the decrease of the degree of crystallinity of cotton.

The effect of the chain length of crosslinkage on the tensile properties of cotton was discussed. It was expected that polymer chain crosslinkage would be useful to prevent the decrease of tensile strength. When cotton was crosslinked with APO after grafted with acrylic acid, some results to meet our expectation were obtained.

INTRODUCTION

To improve the practical quality of cotton fabrics, the shrink and creaseproof finishes with intermolecular crosslinking agents are commonly utilized. In this case, it is a serious practical problem that the tensile strength of cotton fiber is remarkably decreased with the increase of crease recovery. The cause of this undesirable phenomenon is not yet clarified, so the essential means of prevention is not actualized, but some temporary means have been taken, such as the mercerization of cotton fabric, and the addition of vinyl polymer emulsion or surfactants into the finishing bath. In recent years, accompany with the development of durable press finishing in which high concentration of the crosslinking agent is used, this problem has become more serious and various preventive means have been attempted.

Under these circumstances, considering that it is not only scientifically interesting but also practically important to clarify the fundamental mechanism of the above

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phenomenon, the author wishes to present an opinion from the standpoint of molecular structure.

Though by the crosslinking of cotton fabric not only the tensile strength but also the abrasion resistance are damaged, only tensile strength will be discussed in this paper to avoid complication.

As shown in Table 1, though the tensile strength of rayon is not decreased by crosslinking, that of cotton and linen are remarkably decreased, although all of these are alike cellulosic fibers. It is suspected that the consideration of the mechanism of this discrepancy may give an effective indication to solve the problem of the decrease of tensile strength by the crosslinking of cotton.

Meanwhile, as well-known for a long time, the tensile strength of natural cellulose fiber such as cotton and flax increases by wet, contrary to rayon. As described later, it was found that this anomaly of wet tensile strength disappered as the degree of polymerization or crystallinity was decreased. It is supposed that this fact may be instructive to the problem of the decrease of tensile strength of cotton by crosslinking.

Table 1. Effect of Urea Formaldehyde Resin Treatment on Tensile Strength of Various Fabrics.[2]

Fiber type	Rayon		Fortisan	Cotton	Linen
	Spun	Fil.			
Tensile strength change (Aver. W+F) (%)	+9	+7	+1	−13～−20	−36

UF conc. 12% (Fortisan, 24%)
Catalyst : amine HCl 0.5% (Fortisan, 1%)

THE DECREASE OF THE TENSILE STRENGTH OF COTTON BY THE INTERMOLECULAR CROSSLINKING

As well-known, the crease recovery of cotton fabric is remarkably increased by the so-called resin finishing using dimethylol urea (DMU). trimethylol melamine (TMM), dimethylol ethyleneurea (DMEU), *etc.*

M. Imai and W. Tsuji[1] examined the relation between the resin content (add-on) of resin finished cotton fabric using DMU, TMM and DMEU. The relation was also examined in the case of resin removing, when the resin was dissolved off from the finished fabric which contained 20 wt % of resin, by heating it in mixed aqueous solution of 1.5% phosphoric acid and 5% urea at 50°C for various times. The results obtained are shown in Fig. 1.

As shown in Fig. 1, in the cases of DMU and TMM crease recovery values decreased to that of untreated fabric, when a little quantity of resins was removed, though large quantity of resins still remained in the fabrics. This fact gives fairly strong support to the opinion that the crease resistant effect is caused not by the resin deposition in the fiber, but by the crosslinking between resin and cellulose molecule. In the case of DMEU the decrease of crease recovery by the removal of resin is not so steep. This perhaps is due to the larger density of crosslinking. Figure 2 shows the relation

of tensile strength and resin content in the case of DMEU. It is shown that the tensile strength changes approximately corresponding to the change of crease recovery. Considering together these facts, it is suggested that the decrease of tensile strength is caused by the formation of intermolecular crosslinking.

On the effect of crease proof finish upon the tensile strength of cellulosic fabrics, numerous experimental results have been obtained. As one example, Table 1 shows a result in the case of ureaformaldehyde resin finishing[2].

Tensile strengths of regenerated cellulose fibers such as rayon or Fortisan are not decreased by the finishing, but rather somewhat increased. On the contrary, the tensile strengths of cotton and linen are remarkably decreased. As the cause of this discrepancy, the following view is generally supported.

Cotton and flax have large degree of polymerization and crystallinity and rather narrow, restricted non-crystalline regions. Therefore, the mobility of molecular segment in the non-crystalline region is restricted. When tension is given to them, the even distribution of tensile stress is restrained and the stress concentration is apt to occur. If crosslinkings are formed in the non-crystalline region, the mobility of molecular segment is more restricted and stress concentration increased, thus decrease of tensile strength is caused.

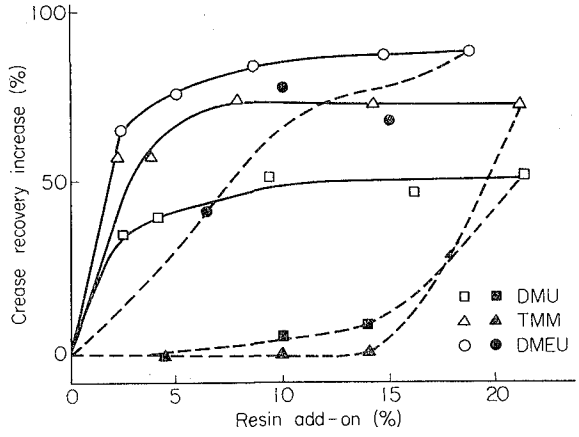

Fig. 1. Relation between crease recovery of cotton fabric and resin add-on.[1]
--- After decomposition of resin
(1.5% phosphoric acid, 5% urea, 50°C)

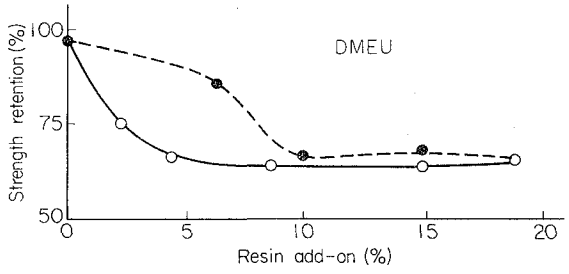

Fig. 2. Tensile strength retention of DMEU treated cotton fabrics.[1]

On the other hand, rayon has wide non-crystalline region and the mobility of molecular segment in non-crystalline region is comparatively large. Therefore, the tensile strength of rayon does not suffer unfavorable effect by crosslinking, but rather some increases are given due to the profitable effect of such as the prevention of molecular slip off.

EFFECT OF THE DEGREE OF POLYMERIZATION AND CRYSTALLINITY ON THE TENSILE PROPERTIES OF COTTON

As above-mentioned, the effect of the formation of crosslinking on the tensile strength is opposite as for cotton and rayon. Hereupon, the well-known fact is reminded that by water wetting the tensile strengths of cotton and flax fibers are not decreased unlike rayon, but rather somewhat increase.

This mechanism is generally interpreted as following. As above described, since the non-crystalline regions of cotton and flax are narrow, mobility of molecular segment is restricted and the concentration of tensile stress is apt to occur. If water is present, it plays a role of lubricant and has the effect of prevention of stress concentration, and thus the increase of tensile strength is caused. On the contrary, in the case of rayon the effect of water to cause molecule slip off is rather predominant than the effect to decrease the stress concentration, and thus the decrease of tensile strength is caused.

Thus, considering together with the above mentioned mechaism of the decrease of tensile strength of cotton and flax by crosslinking, it is presumed that the anomalous changes of tensile strength of cotton and flax both in the cases of crosslinking and water wetting are caused by the same molecular mechanism. Therefore, it is expected that the suggestion will be given to prevent the decrease of tensile strength by crosslinking, if the effect of molecular structure factors on the anomaly of wet tensile strengths of cotton and flax will be examined.

As the molecular structure factors of fiber, molecular orientation, degree of polymerization and crystallinity are important. As in the case of Fortisan and special super high tenacity rayon that have high molecular orientation the ratios of wet and dry tensile strengths are fairly lower than 100%, molecular orientation is not considered as the cause of the anomaly of wet tensile strength.

The degree of polymerization of cotton cellulose is above 2000, and widely larger than 300-500 of rayon. It is interesting to examine whether the anomaly of wet tensile strength of cotton disappears if the degree of polymerization of cotton is decreased near to that of rayon, or whether the anomaly of wet tensile strength appears if the degree of polymerization of rayon is increased up to that of cotton. So far as published, the highest degree of polymerization of rayon is several hundred and in that case the wet and dry tensile strength ratio is larger than normal rayon but still fairly lower than 100%. Considering from the experimental results of Negishi described below, it is interesting if the rayon can be made having the degree of polymerization of about 1000 and proper degree of crystallinity and molecular orientation, though it is still in the future.

Another way is to decrease the degree of polymerization of cotton. As it is

Table 2. Relation between Degree of Polymerization and Tensile Strength of Cotton Fiber at Various RH.[3]

		$\overline{P}$	Tensile strength (g/d)		
			RH 30%	65%	Wet
Raw cotton		2320	3.72	4.74	4.74
Oxidation time* (hrs)	2	1020	3.74	4.80	4.65
	5	710	2.68	3.00	2.95
	24	418	2.49	2.38	2.55
	48	306	2.02	2.22	1.67
	96	211	1.80	1.44	1.02

* Treated with sodium hypochlorite

impossible for the present to obtain in nature the cotton having low degree of polymerization, the next best way is to be to decrease artificially the degree of polymerization of cotton. On this problem the research of Negishi[3] is remembered.

In his work the degrees of polymerization of cotton and ramie were decreased to various degree by hydrolysis or oxidation, and the stress-strain curves were determined in various relative humidities at 20°C and the tensile strength, elongation and Young's modulus were calculated. Some results for cotton are shown in Table 2.

As shown in Table 2, the anomaly that the tensile strength of cotton increases with the increase of humidity disappears with the decrease of the degree of polymerization. If the degree of polymerization of cotton is decreased below several hundreds, the change of its tensile strength with humidity becomes nearly similar to rayon. Almost the same results were found on cotton and ramie in various conditions of decomposition. Therefore, it is probable that the degree of polymerization may be one factor relating to the anomaly of wet tensile strength of cotton or ramie.

Connecting this with the problem of the decrease of tensile strength of cotton by the crosslinking, it seems interesting to examine the effect of the crosslinking on the tensile strength of cotton of which the degree of polymerization is previously decreased, though such a research has not been carried out. Recently, it was reported[4] that the degree of polymerization of cotton fabric was decreased till about 1200 by hydrolysis with hydrochloric acid or oxidation with natrium hypochlorite to prevent the stress concentration, then crosslinking was given, but the effect to prevent the decrease of the tensile strength was not distinct. Though still lower degree of polymerization seems to be desirable, it may be difficult to obtain favorable result as the decrease of the tensile strength may accompany with the decrease of the degree of polymerization

Now, the next problem is the effect of the degree of crystallization. The value of the degree of crystallization estimated by x-ray diffraction is about 70%, which is far higher than the value of rayon of about 40%. The researches on the decrystallization of cotton to decrease remarkably the degree of crystallization of cotton without lowering its mechanical properties have been carried out in U.S.A. since about 1950. Afterward, different from the method in U.S.A. using ethylamine, we developed more practical and effective method using caustic soda solution and acetic

anhydride or acrylonitrile, by which the degree of crystallinity of cotton may be reduced by half. Table 3 shows the properties of cotton fiber decrystallized by caustic soda-acrylonitrile method[5]. The decrease of the degree of crystallization is indicated by the moisture absorption higher than mercerized cotton. The dry tensile strength is increased by the decrystallization, probably dues to the relaxation effect of stress concentration. It is noted that the wet tensile strength is lowered than the dry tensile strength by the decrystallization. Thus, it is presumed that the degree of crystallization also relates to the anomaly of the wet tensile strength of cotton.

Now, it is the interesting problem to examine the effect of the crosslinking on the tensile strength of the decrystallized cotton. On this subject sufficient investigations are not yet carried out, but in a preliminary experiment it was found, as shown in Table 4, that the decrease of the tensile strength of decrystallized cotton seemed to be less than untreated or mercerized cotton, though much more detailed investigations were needed hereafter to ascertain these effects.

In our method of decrystallization cotton fabric is impregnated with 18% NaOH solution and then immersed into acrylonitrile. Slight degree of cyanoethylation of cellulose is occured and the recrystallization during water rinse and drying is prevented. Recently, Gagliardi[6] developed SSX method which consisted of swelling, substitution and crosslinking of cotton, and it was reported that the decrease of the tensile strength of cotton crosslinked by this method was small. The principle of this method seems to be the same as ours above described. Gagliardi showed in Fig. 3(A) the state of

Table 3. Physical Properties of Decrystallized Cotton.[5]

Sample	Moisture content (%)	Tensile str. (g)[c]		Elongation (%)[c]	
		Dry	Wet	Dry	Wet
Untreated	7.5	5.04	5.26	4.8	11.4
Mercerizd[a]	12.0	5.27	5.73	10.5	13.5
Decrystallized[b]	14.5	6.59	4.68	7.5	15.9

a) 18% NaOH, 18°C, 30 min.
b) 18% NaOH, 15°C, 30 min.; acrylonitrile, room temp., 15 min.; Nl.61%, degree of cyanoethylation 6.59 mole %
c) Tensile properties of fiber taken from warp yarn.

Table 4. Properties of Resin Treated Cotton Fabrics.

	Sample	Crease recovery (%)		Tensile str. (Kg)
		Dry	Wet	
No resin	Control	35	26	9.4
	Mercerized	30	36	10.0
	Decrystallized*	18	33	10.2
DMEU (10%)	Control	76	64	4.1
	Mercerized	80	71	4.3
	Decrystallized*	71	75	5.0

* Degree of cyanoethylation : 6 mole %

crosslinked non-swollen cotton and in Fig 3(B) showed the cotton after swelling and introducing some substituting groups. He presumed that the inner structure expanded by swelling was permanently maintained by the aid of the introduced substitution groups It was concluded that due to the expanded inner structure even distribution of crosslinking and relaxation of stress concentration were caused and as the result the decrease of tensile strength was prevented. This idea just coincides with ours.

Table 5 shows one example of the results of Gagliardi's research. Cotton fabric swollen with caustic soda solution was hydroxyethylated and then crosslinked with dimethylol ethylene urea. The decrease of abrasion resistance and tensile strength was less than untreated cotton.

By the way, Gagliardi showed in his paper the interesting experimental result as following. If cotton fabric was immersed into 50% aqueous solution of urea and dried, the Monsanto crease recovery angle (MCRA) was remarkably decreased, while the tensile strength was highly increased as shown in Table 6.

It was presumed that, owing to the break down of intermolecular hydrogen bonds by urea the elasticity of cotton was decreased and the tensile strength was increased due to the relaxation of stress concentration. It was found that if urea was removed by water washing both original values were restored. Similar results were found with other various crosslinking agents. Anyhow, it is interesting that tensile strength of cotton can be increased as much as 50% by such a simple treatment.

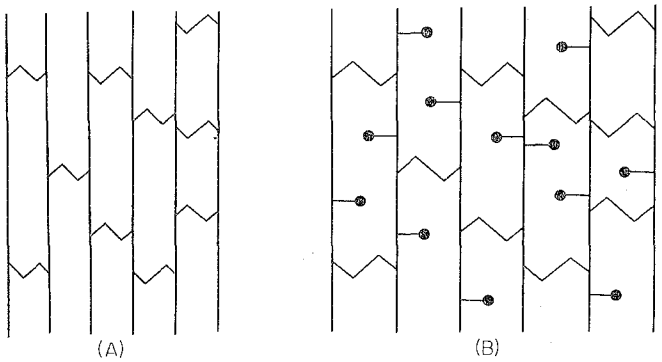

Fig. 3. Crosslinking of cotton cellulose.[6]

Table 5. Crosslinking of Hydroxyethylated Cotton Fabric with 5% DMEU[6]

Pretreatment of fabrics		MCRA (W+F)° Dry	MCRA (W+F)° Wet	Stoll Flex W	Tensile (lb/in)	Retention (%)
Untreated		134	140	738	54	100
Untreated, DMEU only		258	240	557	29	54
Caustic control		259	258	911	33	61
Ethoxyl. (%)	1.64	239	270	920	46	85
	3.30	237	293	919	42	78
	7.45	288	307	751	41	76

Table 6. Influence of Urea on Wrinkle Resistance and Tensile Strength of Cotton Fabrics.[6]

Treatment (5% solids)	MCRA (W+F)°			Tensile strength (lbs/in)		
	Initial	Urea in[a]	Urea out[b]	Initial	Urea in[a]	Urea out[b]
None	162	68	172	112	171	107
Triazone	272	126	260	67	107	66
DMEU	262	102	252	68	110	73
DMU	257	108	242	66	113	68
APO	250	126	253	76	123	72
TMM	260	109	254	73	122	67

a) Impregnated with 50% urea solution and dried.
b) Urea is removed by washing.

THE EFFECT OF THE LENGTH OF CROSSLINKAGE ON THE TENSILE STRENGTH OF CROSSLINKED COTTON

The formation of intermolecular crosslinking is an effective way to improve the elasticity of fiber. Here the effect of the length of crosslinkage on the decrease of tensile strength of cotton is a problem to be examined. Though many researches have been carried out on this problem, their conclusions were not always definite. In some researches favorable effects were shown of long chain of crosslinking to prevent the decrease of tensile strength, but in another works it was not distinct. On this subject the experimental method of treating with crosslinking agents of different chain lengths is a question. For example, in former researches organic solvent solutions of crosslinking agents having different alkyl chain lengths were mainly used. Depending on the kind of solvent and the chain length of crosslinking agent, the location or distribution of the crosslinkage will be different, so it will be difficult to evaluate impartially the effect of the chain length of crosslinkage. But in recent years, various treating methods using water as solvent of crosslinking agents have been developed. For example, Table 7[7] and Table 8[8] are the results of experiments using as crosslinking agent chloromethyl ether pyridinium salts and bishydroxyethyl sulfones having different chain length. Though not fully definite in either cases, some tendencies are seen that the decrease of tensile, tear and abrasion strengths is somewhat prevented as the chain length of crosslinkage increases.

As the ground of our interest in the effect of the chain length of crosslinkage we have following experimental result. The elasticity of vinylon (polyvinyl alcohol fiber) is unsatisfactory, so various methods of improvement have been studied. The formation of crosslinking was one of them. As shown in Table 9[9], by the crosslinking with dialdehyde such as acetaryl monosulfide or dimethylol ethylene urea, the tensile recovery of vinylon is satisfactorily increased and resistance to hot water was given, but the knot strength was highly decreased. This indicates that the fiber becomes too brittle.

But we found an interesting result on this subject. Once we made a kind of vinylon by mix spinning of ordinary polyvinyl alcohol (PVA) and PVA decomposed

with periodic acid. As well known, periodic acid breaks down 1,2-glycol linkage and aldehyde group is formed. Therefore, if ordinary PVA which has a small quantity of 1,2-glycol linkage is reacted with periodic acid, PVA is decomposed and PVA that has aldehyde group at one or two ends of molecular chain is produced. Fiber made by mix spinning of such a decomposed PVA with ordinary PVA and aftertreating with sulfuric acid was found to have high tensile recovery and resistance to hot water, and it was noted that no decrease of knot strength was caused as shown in Table 9.

Table 7. Effect of Crosslinking with Bis Chloromethyl Ether Pyridinium Chlorides on Properties of Cotton Fabrics.[7]

Cell·O·CH_2O·R·OCH_2·O·Cell

R	No. of atoms in bridge	Weight add-on(%)	Crease recov. (W+F)[c]	Strength change (%)	
				Tensile	Tear
Control	—	—	140	0	0
CH_2CH_2	8	4.5	253	−47	−47
$CH_2CH_2OCH_2CH_2$	11	6.3	257	−47	−58
$(CH_2)_5$	11	6.3	260	−48	−53
$(CH_2)_{10}$	16	9.9	255	−42	−16

Table 8. Effect of Crosslinking with Bis Hydroxyethyl Sulfones on Physical Properties of Cotton Fabrics.[8]

$HOCH_2CH_2SO_2$·R·$SO_2CH_2CH_2OH$

R	No. of atoms in bridge	Conc. owf (%)	Crease recov. (W+F)°		Breaking strength (lb) W	Tear str. Elmendorf W	Abrasion resist. (cycles) W
			Dry	Wet			
Control	—	—	155	165	51.6	42.4	773
$(CH_2)_5$	11	5	242	253	34.6	36.2	658
$CH_2CH_2OCH_2CH_2$	11	5	250	270	30.5	26.8	421
$(CH_2CH_2O)_2CH_2CH_2$	14	5	230	260	29.1	28.8	400
$(CH_2CH_2O)_5CH_2CH_2$	23	3	210	240	36.8	32.0	436
None*	5	4.6	230	258	33.8	29.0	376

* Commercial bis(hydroxyethyl) sulfone $HOCH_2CH_2SO_2CH_2CH_2OH$

Table 9. Properties of Crosslinking PVA Fiber.[9]

Crosslinking agent	Tensile recovery (%)		Knot/normal Str. ratio (%)	Shrinkage in boiling water (%)
	3% elong.	5%		
Vinylon (Standard)	50～65	40～50	70～75	<5
Acetaryl monosulphide[a]	70	63	～20	<5
DMEU	93	90	—	5
	62	58	27	2.8
PVA decomposed with HIO_4[b]	85	82	100	4.7

a) $(C_2H_5O)_2$·CH·CH_2·S·CH_2·CH·$(OC_2H_5)_2$

b) Mix spinning with ordinary PVA.

The reason is not definite, but it is presumed that, by the reaction of aldehyde groups on the chain end of the decomposed PVA with OH groups of other PVA molecule in non-crystalline region, a kind of long chain (polymer) crosslinkage was formed, which gave rise to such a interesting effect.

Considering such a result, polymer crosslinkage may be a subject worth investigation to prevent the decrease of tensile strength by crosslinking. It was found by Negishi and the author that the elasticity of cellulose fiber was increased by grafting of alkyl acrylate without decrease of tensile strength. It was considered that a kind of polymer linkage was formed by the entanglement of grafted chain.

Now, the useful method to form polymer crosslinking in fiber is the use of graft copolymerization. Thus, polymer crosslinking may be formed when the monomer which has a functional group is grafted and crosslinking agent is reacted to the functional groups of grafted chain.

We have carried out the research on the cotton grafted with functional monomer such as acrylamide, acrylic acid or glycidyl methacrylate and then reacted with crosslinking agent.[10] In these researches it was found that by the crosslinking after grafting dry and wet crease recovery were remarkably increased, but in most cases tensile strength was fairly decreased. But, as shown in Table 10, it was found that the crease recovery was increased fairly well with slight decrease of tensile strength, when cotton was crosslinked with tris(1-aziridinyl) phosphine oxide (APO) using zinc borofluoride as catalyst. So it is expected that the research in this way may be promising and further investigation will be carried out.

Table 10. Treatment of Acrylic Acid Grafted Cotton with APO.

Graft (%)	APO conc. (%)	$\frac{Zn(BF_4)_2}{APO}$(%)	Crease Recovery (%)		Tensile str. (Warp yarn) (g)
			Dry	Wet	
0	0	0	33.0	35.0	310~320
22.2	0	0	30.4	32.1	304
0	15	5	78.1	74.2	247
22.2	15	5	65.9	70.0	227
0	5	3	71.1	62.5	237
22.2	5	3	69.4	47.5	272
0	5	1	66.5	40.2	268
22.2	5	1	67.1	49.7	292
0	3	1	59.2	50.3	269
22.2	3	1	67.9	55.9	301

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